

# PATENT SPECIFICATION

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## (54) PROCESS FOR THE PRODUCTION OF RELIEF USING PHOTOPOLYMERISABLE POLYMERS

(71) We, AGFA-GEVAERT AKTIEN-  
 GESELLSCHAFT, a body corporate  
 organised under the laws of Germany, of 509  
 Leverkusen, Germany, do hereby declare the  
 invention, for which we pray that a patent  
 may be granted to us, and the method by  
 which it is to be performed, to be particu-  
 larly described in and by the following state-  
 ment:—

This invention relates to a process for the  
 production of relief images using photopoly-  
 merisable polymers.

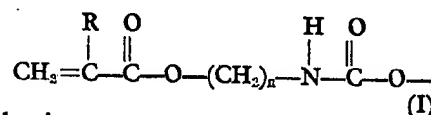
Numerous polymer systems which are  
 hardened by the action of light thus forming  
 insoluble cross-linked coatings are known.  
 These systems are used particularly in re-  
 production work, for example, for the pro-  
 duction of relief printing plates, printed cir-  
 cuits and stereotype printing blocks. They  
 may generally be divided into two different  
 types. In the first type of polymers, each  
 light quantum leads to only one cross-link-  
 ing position. Polycinnamic acid esters and  
 polymers which can be photo cross-linked by  
 diazides are polymers of this type. These  
 systems are generally not very sensitive to  
 oxygen. The second type of polymers which  
 are hardened by light contain vinyl groups  
 and are cross-linked by addition polymerisa-  
 tion via these vinyl groups, only a few quanta  
 of light being sufficient to produce a large  
 number of cross-linking positions. The de-  
 mand for these systems is constantly increas-  
 ing in spite of their high sensitivity to oxy-  
 gen because their sensitivity to light, includ-  
 ing light from the visible region of the spec-  
 trum, is many times greater than the other  
 type, especially if suitable sensitizers are used.

The photopolymerisation systems pre-  
 viously used for reproduction purposes are  
 not free from disadvantages, apart from their  
 sensitivity to atmospheric oxygen. Photopoly-  
 merisable systems for reproduction purposes  
 must be non-tacky and have a certain mecha-

nical strength even before they are cross-  
 linked. For this reason it has previously been  
 customary to use mixtures of relatively high  
 molecular weight uncross-linked polymers and  
 vinyl compounds of high molecular weight,  
 e.g. acrylic acid esters of polyhydric alco-  
 hols such as pentaerythritol or trimethylol-  
 propane. The layers obtained from these  
 systems after photocross-linking, however,  
 undergo severe swelling and moreover the  
 unexposed coatings rapidly become brittle in  
 the presence of atmospheric oxygen. The  
 photopolymerizable vinyl groups, e.g. acryloyl  
 units can also be attached to the polymer  
 chain. Such systems are very suitable for  
 reproduction materials but their preparation is  
 difficult since rather extreme reaction condi-  
 tions are required which necessitate the addi-  
 tion of inhibitors such as hydroquinone or  
 copper salts in order to prevent premature  
 gelling of the reaction mixtures. If these  
 additives are used, the products obtained show  
 little light-sensitivity in the subsequent photo-  
 cross-linking reaction.

It is among the objects of the present  
 invention to provide polymer systems capable  
 of being polymerised by vinyl polymerisation  
 initiated by electrons or actinic radiation  
 which would not have the disadvantages men-  
 tioned above.

The present invention provides a process  
 for the production of a photographic relief  
 image in which a film comprising at least one  
 photopolymerisable polymer which contains  
 at least two recurring groupings of the fol-  
 lowing formula I



wherein

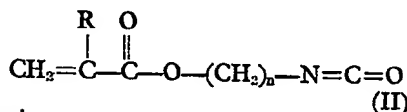
R is a hydrogen atom or an alkyl group  
 containing 1 to 4 carbon atoms, and

[Price 33p]

n is an integer from 1 to 6, is imagewise exposed to electrons or actinic radiation to polymerise the polymer in those areas which have been so exposed, and the unexposed areas of the said image are removed.

Polymers which contain the above recurring units at least twice per structural unit having a molecular weight of around 1000 are preferred. Particularly useful are photopolymerisable polymers having a molecular weight of between 10,000 and 100,000.

The photopolymerisable polymers of the present invention are prepared by reacting known polymers which contain at least two hydroxyl groups with vinyl monomers containing isocyanate groups represented by the following formula:



wherein

R and n have the meaning as in the formula of the polymer referred hereinbefore.

The hydroxyl polymers used may be either natural products or synthetic high molecular weight compounds. Suitable natural polymers are cellulose, starch, gelatin or derivatives of these natural substances such as partly esterified or etherified cellulose. Suitable synthetic polymers are polyvinyl alcohols or copolymers which contain vinyl alcohol units in a polymerised form. These polymers may contain unreactive polymer components consisting of any other units of polymerisable monomers, especially vinyl monomers, e.g. ethylene, propylene, butylene, butadiene, isoprene, vinyl chloride, vinyl esters of monobasic organic acids, vinyl ethers, especially vinyl isobutyl ether, acrylic or methacrylic acids or their derivatives such as esters, especially esters with aliphatic or cycloaliphatic alcohols having up to 8 carbon atoms, nitriles such as acrylonitrile, maleic acid anhydride or styrene.

Polycondensates with active hydrogen atoms, especially with alcoholic hydroxyl groups are also suitable, for example polyesters of polybasic aliphatic or aromatic carboxylic acids with polyhydric alcohols, polyurethanes which contain hydroxyl groups or epoxy resins which contain hydroxyl groups.

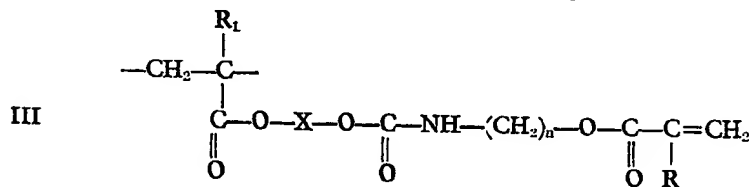
The polymeric reactants should preferably have an average molecular weight of above 1000. The most suitable average molecular weight for any given purpose can easily be determined by a few simple tests. The optimum molecular weight range also depends, of course, on the nature of the polymer.

It is preferred to use polymers which may be obtained by the polymerisation of hydroxyalkyl esters of acrylic acid or of  $\alpha$ -alkyl-substituted acrylic acids such as methyl methacrylic acid or by copolymerisation of these compounds with other vinyl compounds. Suitable hydroxyalkyl esters are the monoesters of the aforesaid acids with ethylene glycol, propylene glycol, propane-1,3-diol, butanediol, diethylene glycol and higher polyethylene glycols.

The polymers are preferably dissolved in solvents which do not react with isocyanates under the reaction conditions employed in this process, such as hydrocarbons, halogenated hydrocarbons, esters, ketones or ethers, and are reacted with the unsaturated isocyanate either without the addition of any other substances or with the addition of the usual catalysts used for promoting urethane formation, such as tertiary amines.

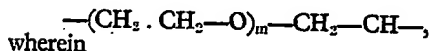
The vinyl monomers containing isocyanate groups may be obtained by the methods described in US Patent Specification 2,821,544. Isocyanatoethylacrylate and isocyanatoethyl methacrylate are preferred. Hydroxyl polymers reacted with these compounds exhibit particular utility as light-sensitive layers.

The polymerisable polymers based on polymeric hydroxyalkyl acrylates comprise a polymer chain containing recurrent units of the following formula:



wherein

X represents a divalent aliphatic radical which may be interrupted by oxygen atoms, such as ethylene, propylene, isopropylene, butylene, radicals of the formula



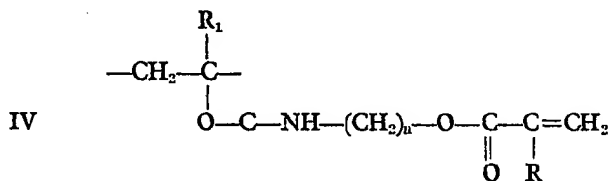
m represents an integer which is either 1 or greater than 1, and preferably 1 to 3;

R<sub>1</sub> represents hydrogen or alkyl groups having 1 to 4 carbon atoms, preferably methyl and

R and n have the meaning defined hereinbefore.

When polymers with vinyl alcohol units or units of derivatives of vinyl alcohol, such as polyvinyl alcohol or partly or completely saponified copolymers of ethylene with vinyl acetate are used for preparation of the poly-

merised polymers, the polymers consist of carbon chains which contain recurrent units of the following formula, wherein R, R<sub>1</sub> and n have the same meaning as in the previous formulae:



Preparation of the polymerisable polymers may be carried out as follows: A vinyl monomer which contains hydroxyl groups may be first polymerised in known manner in an inert solvent, either alone or in combination with up to 95% by weight of other vinyl monomers.

The resulting polymer solution is cooled to room temperature and mixed with the isocyanate which contains vinyl groups with the exclusion of moisture but in the presence of atmospheric oxygen. In this mixture, the molar quantity of isocyanate should not exceed the hydroxyl group content of the polymer. The reduction in the isocyanate absorption at 2275–2250 cm<sup>-1</sup> in the infra-red spectrum of the reaction mixture serves as indication of the degree of conversion between hydroxyl groups and isocyanate-containing vinyl compounds (K. NAKANISHI, *Infrared Absorption Spectroscopy*, Holden-Day, Ind. San Francisco (1961) page 28). The reaction is usually completed within a few days even without the addition of catalysts such as tertiary amines but additions of less than 1% of triethylamine may shorten the reaction time to a few hours.

When the reaction has been completed, the reaction solution of the polymerisable polymer which contains urethane groups may be used directly for the production of the photosensitive layers. In order to improve the light-sensitive, the solution may be sensitized with 0.1 to 10% by weight based on the weight of the photopolymerisable polymer of the usual photoinitiators.

Suitable photoinitiators are described by J. C. BLOINGTON in "Radical Polymerization", published by Academic Press New York, 1961. Compounds of this kind include hydrazones, 5-membered nitrogen, containing heterocyclic rings, mercapto compounds, pyrylium or thiopyrylium salts, thioxanthrones, dyestuff-redox systemes, acridine and phenothiazine compounds as described for example in German Offenlegungsschrift No. 2,027,467.

Dimers of lophine for example of 2,4,5-triphenylimidazole are also suitable. Compounds of this type are described in British Patent Specification Nos. 997,396 and

1,047,569. Furthermore, α-phenylethyl alcohols may also be used, as described in German Offenlegungsschrift 2,015,711. Reference is further made to polynuclear quinones such as anthraquinone, 2-methyl anthraquinone, 2 - tert. - butyl anthraquinone, anthraquinone - 2 - carboxylic acid butyl-ester, phenanthraquinone. Suitable photoinitiators are also benzophenone derivatives such as described in British Patent Specification No. 1,242,988 or components of the benzoin series such as benzoin, benzoin ethers or hydroxy methyl benzoin which are described in British Patent Specification Nos. 1,209,867; 1,229,082 or 1,265,604 or U.S. Patent Specification Nos. 3,639,321; 3,657,088; 3,607,693 or 3,636,026. The photoinitiators can be used alone or in admixture with other initiators.

It may be advantageous to improve the storage stability by adding thermal inhibitors such as phenol derivatives or hydroquinone derivatives or stabilizers such as copper salts. Other solvents, plasticizers, coating acids, dyes or other fillers which should not absorb light of the spectral region of the light used for initiating the photopolymerization as well as inert polymers may also be added.

The solution is applied to the desired layer support by immersion, spraying, casting, roller application centrifuging or by any other of the usual application processes.

The coating obtained is solid but is still soluble in most organic solvents and can be polymerised using light or other actinic radiation either directly or after it has been transferred to another layer support. It is especially advantageous at this stage to exclude atmospheric oxygen which has an inhibiting effect. This can be achieved by carrying out the exposure to light in a vacuum or under a protective atmosphere of nitrogen or preferably by protecting the light-sensitive layer with a transparent plastics foil. After the polymerisation of the exposed areas of the coating, the unexposed areas of the layer are washed out with an organic solvent.

Suitable solvents for this purpose are particularly those which may also be used for application of the layer but practically any solvents in which the unpolymersed polymer

is soluble and the exposed areas of the layers are insoluble may also be used, such as chlorinated hydrocarbons, higher alcohols, esters or aromatic hydrocarbons. The polymerised insoluble portions of the layer adhere to the layer support and resist all the customary etching solutions such as dilute nitric acid and iron-III chloride solutions as well as metal deposition in the usual baths.

Suitable layer supports are metal foils of copper, aluminium, zinc, magnesium, steel, paper, glass, or foils of polymers, such as cellulose ethers, polyvinyl acetate, polyphenylolalkanes, polyesters, especially those based on polyethylene terephthalate, polyamides, e.g. nylon. Materials which have a mesh structure such as metal mesh may also be used as supports. With suitable polymers it is also possible to produce selfsupporting films.

The photopolymerisable layers according to the invention may be used for the production of relief images or printing formes for relief printing, intaglio printing or planographic printing. They may be used especially for offset printing processes, screen printing processes, lithographic printing plates or any other printing processes which require a relief image as well as photogravure processes. The layers according to the invention are also suitable for the production of photoresists to make printed circuits, etched mouldings, mouldings by the electro-forming process and integrated microcircuits.

Exposure of the layers produced according to the invention is carried out with the usual sources of light used in reproduction work, such as carbon arc lamps, Xenon lamps and high pressure mercury lamps which advantageously provide a particularly effective portion of ultraviolet light for polymerization in addition to visible light.

The polymerisation reaction may be initiated by electrons and actinic radiation. The term "actinic radiation" as used herein includes high energy radiation such as X-rays and  $\gamma$ -rays as well as, of course, visible light.

The following Examples illustrate the invention.

#### Example 1

##### Preparation of the polymer:

400 ml of tertiary butanol were refluxed under a nitrogen atmosphere in a 2-litre three necked flask equipped with stirrer, a reflux condenser and dropping funnel. A mixture of 288 g of hydroxypropyl methacrylate, 150 g of methyl methacrylate, 250 g of methylacrylate, 100 g of tertiary butanol and 1.5 g of benzoyl peroxide was added dropwise in the course of 5 hours. When this operation was completed, another 0.5 g of benzoyl peroxide in tertiary butanol was added and the mixture was kept at reflux for 4 hours. After removal of tertiary butanol by evaporation,

which was carried out partly under vacuum, the polymer was freed from remaining solvent by drying in a vacuum drying cupboard at 15 mm/50°C. 580 g of a colourless solid resin were obtained.

480 g of the polymer were dissolved in methylene chloride to give a concentration of 30% by weight, and 194 g of isocyanatoethylmethacrylate were added at room temperature with stirring in the course of 30 minutes. The mixture was kept at room temperature for another 48 hours.

##### Light-sensitive material:

The solution prepared as described above was sensitized with 3% by weight (based on the dry film forming polymer) of 2-chloromethyl-anthraquinone and coloured by the addition of 0.5% by weight of Sudan blue. An aluminium foil was coated with this solution on a whirling coater and dried in the usual way. After drying, the light-sensitive layer has a thickness of 28 to 30  $\mu$ . The layer was then covered with a 30  $\mu$  thick polyethylene foil to protect it against oxygen which acts as a polymerisation inhibitor.

##### Processing:

The above material was exposed through an original for 4 minutes in a Chem-Cut exposure apparatus. This exposure corresponds to approximately 2 minutes' exposure with a carbon arc lamp (42 Volt, 30 Amp.) at a distance of 45 cm. After removal of the protective foil, the unexposed parts of the layer are washed out with a mixture of ethyl acetate and trichloroethylene. A sharp relief image of the original is obtained.

#### Example 2

##### Preparation of the polymer:

Using a method analogous to that of Example 1, a mixture of 95 g of hydroxypropylmethacrylate, 100 g of methyl methacrylate, 42.2 g of butyl acrylate, 100 g of methylethyl ketone and 3 g of azoisobutyric acid dinitrile was added dropwise in the course of 6 hours to 800 ml of methyl ethyl ketone which was boiling under reflux. After the further addition of 1 g of azoisobutyric acid dinitrile, the reaction mixture was again heated under reflux for 5 hours. 500 g of the polymer solution were concentrated to 250 g by distilling off the solvent, and 45 g of isocyanatoethyl methacrylate were added with stirring at room temperature in the course of 30 minutes.

##### Light-sensitive material:

After 48 hours at room temperature, the polymer solution was sensitized with 3.5% by weight of 2-tertiary-butyl anthraquinone, based on the amount of dry film-forming polymer. This solution was used for coating a 30  $\mu$ m thick polyester foil and the

coating was then transferred to a thin copper foil at 120°C using a laminating roller. The thickness of the pure photopolymer layer was 35  $\mu$ .

#### 5 Processing:

The material described above was exposed through the polyester foil for 4 minutes through a 0.15 grey step wedge in a Chem-Cut exposure apparatus.

10 This exposure corresponds to approximately 2 minutes exposure with a carbon arc lamp (42 Volt, 30 Amp), at a distance of 45 cm. After removal of the covering foil, the unexposed parts of the layer are washed off with a mixture of ethyl acetate and i-propanol. A sharp relief image of 12 steps of the original is obtained.

#### Example 3

20 A sample of the material of Example 1 was stripped of its polyethylene protective foil and then exposed for 4 minutes in a Chem-Cut exposure apparatus which had been washed several times with nitrogen. The original through which it was exposed was a 0.15 grey step wedge.

25 After washing off the unexposed areas of the layer with a mixture of ethyl acetate and trichloroethylene, a sharp relief image of 10 step wedges of the original was obtained.

#### 30 Example 4

A sample of the material of Example 2 was exposed through an original for 4 minutes in an exposure apparatus which had been washed several times with nitrogen. The non-light struck areas are washed out with a mixture of isopropanol and ethylacetate. The resulting sharp relief image of the original could be transferred when dry to a copper-Pertinax foil by means of a laminating roller heated to 120°C.

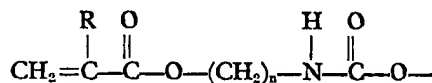
#### Example 5

45 42.4% by weight of a saturated polyester based on phthalic acid and trimethylolpropane and having an acid number of 3 and OH number 263 (viscosity of a 50% by weight solution in ethyl glycol acetate: 850 cp) were dissolved in 100% by weight of ethyl acetate, 0.5 part by weight of triethylamine was added and the components were mixed with 31 parts by weight of isocyanatoethylmethacrylate with stirring at room temperature. After 2 days at room temperature, the reaction was completed.

Production of a light-sensitive material and further processing was performed as in Example 2. A sharp relief image was again obtained.

The photopolymerisable polymers used according to the process of the present invention are more fully described and claimed in co-pending application No. 19136/72 (Serial No. ).

The co-pending application provides a polymer containing per molecule at least two groups of the general formula:—

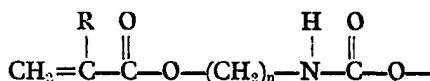


in which

R is a hydrogen atom or an alkyl group with 1 to 4 carbon atoms; and  
n is an integer from 1 to 6.

#### WHAT WE CLAIM IS:—

1. A process for the production of a photographic relief image in which a film comprising at least one photopolymerisable polymer which contains at least two recurring groupings of the following formula 1



wherein

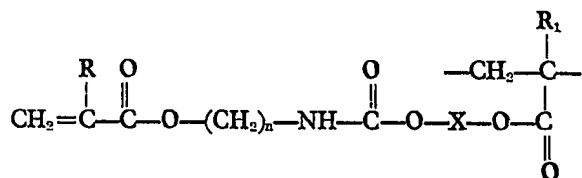
R is a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms, and  
n is an integer from 1 to 6, is imagewise exposed to electrons or actinic radiation to polymerise the polymer in those areas which have been so exposed, and the unexposed areas of the said image are removed.

2. A process as claimed in Claim 1 in which the film is supported by a layer support.

3. A process as claimed in Claim 1 or Claim 2 in which the unexposed areas are removed by washing with an organic solvent.

4. A process as claimed in any of Claims 1 to 3 in which in the formula R is a methyl group.

5. A process as claimed in any of Claims 1 to 4 in which the polymer comprises at least two recurring units of the formula:—

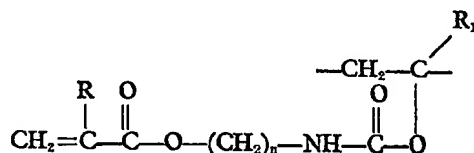


in which

X represents a divalent aliphatic radical,  
R and R<sub>1</sub>, which may be the same or different, are hydrogen atoms or alkyl groups containing 1 to 4 carbon atoms, and

n is an integer from 1 to 6.

6. A process as claimed in any of Claims 1 to 4 in which the polymer comprises at least two recurring units of the formula:—



wherein

R, R<sub>1</sub> and n are as defined in Claim 3.

7. A process as claimed in any of Claims 1 to 6 in which the polymer comprises at

least two of the said units of formula I per 1000 units of molecular weight.

8. A process as claimed in any of Claims 1 to 7 in which, in the formula I, n is an integer from 2 to 4.

9. A process as claimed in any of Claims 1 to 8 in which the photopolymerisable polymer has an average molecular weight of 10,000 to 100,000.

10. A process as claimed in Claim 1 substantially as herein described with reference to any one of the Examples.

11. A photographic relief image when prepared by a process as claimed in any of Claims 1 to 10.

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